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Wavelengths From Thorium-Halide Lamps

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The present system of international secondary standards of wavelength for spectroscopic measurements is based on interferometric determinations of wavelengths emitted at atmospheric pressure by an electric arc between iron electrodes. Because of the poor quality and uneven distribution of these iron standards they are not suitable for accurate measurement of wavelengths in the spectra of heavier elements, most of which are more complex and consist of much sharper lines than the standards. Quartz-tube lamps containing a small quantity of a thorium halide, when excited by microwaves, emit thousands of uniformly sharp and evenly distributed lines whose wavelengths, or positions in a spectrum, can be determined with about one-tenth the error of locating iron-arc lines. Preliminary values of 222 vacuum wavelengths emitted by a thorium-iodide lamp have been measured relative to 5462.2705 and 4047.7144 A emitted by a similar lamp containing mercury-198. Fabry-Perot interferometers with plate separations of 25, 40, or 50 millimeters were used with a stigmatic grating spectrograph in making these measurements. The thorium wavelengths range from 3288.7356 to 6991.5839 A in vacuum and from 3287.7885 to 6989.6562 A in standard air. The accuracy in relative value of 27 classified thorium lines is tested by means of the combination principle, which indicates that the average error is less than 1 part in 20 million.

1. Introduction

During the past half-century the wavelengths of hundreds of radiations from the iron arc at atmospheric pressure have been measured with interferometers to serve as international standards of wavelength for spectroscopic measurements. The history and results of this activity were summarized in *Wavelengths From Iron-Halide Lamps* [1] [1], in which it was shown that the accuracy of measurement could be increased by a factor of 2 or 3 if the iron lines were emitted by simple lamps containing a trace of iron halide excited, at low pressure and moderate temperature, by microwaves. But the iron arc in air is still the main source of internationally adopted standard wavelengths.

The actual application of the adopted iron standards to wavelength measurements in various spectra is handicapped by two serious defects in the iron-arc spectrum. First, because of the high temperature (6,300° K) of the iron arc and the relatively small atomic number ($Z=26$) and mass ($A=56$) of the iron atom its spectral lines are excessively broadened on account of Doppler-Fizeau effect. Moreover, an electric arc between iron electrodes at atmospheric pressure produces lines of various kinds; strongly self-reversed lines involving low energy levels, diffuse lines involving high energy levels, and unstable lines of variable wavelength due to "pole effect." Second, the distribution of strong or similar lines in the arc spectrum of iron is such that no uniform spacing of wavelength standards is possible, and unduly large gaps between usable standards are unavoidable in certain spectral regions. Consequently many spectroscopists have expressed dissatisfaction with the international standards of wavelength emitted by the iron arc. Thus, Harrison [2] states that the wavelength precision of measurements in the MIT Wavelength Tables has been limited primarily by "the insufficiency of adequate wavelength standards in some spectral regions, particularly of standard lines of suitable intensities." Likewise, Bovey [3] in giving a preliminary list of 6-figure wavelengths of plutonium excited in a furnace complains that "A serious difficulty for accurate measurement has been the width of the iron-arc lines, many of which are several times wider than the emission lines from a furnace." Also Fred and Tomkins [4] in describing the first two spectra of americium to 7 figures, announce that "Most of the uncertainty in the wavelengths is due to the poor quality of the standards, since the agreement in the hfs intervals shows that the line positions can be measured to another decimal place."

Logically the iron-arc standards should have been used only for measuring atmospheric arc and spark spectra of metals lighter than iron, because, other things equal, the heavier atoms emit sharper lines which cannot be measured accurately relative to standards that are broader and badly spaced. When the arc spectrum of cerium ($Z=58$, $A=140$) is photographed beside that of the standard iron arc it is readily seen that all cerium lines are narrower than iron lines, and a comparison with thorium ($Z=90$, $A=232$) or with uranium ($Z=92$, $A=238$) is even more embarrassing for iron. This was observed by Harrison [5], who remarked that "In the extensive series of wavelength measurements made with the automatic comparator, which resulted in the publication of the *Massachusetts Institute of Technology Wavelength Tables*, the most serious limitation on precision was found to arise from the lack of satisfactory standard lines. Measurements on lines in such complex spectra as cerium and thorium, for example, showed much better internal consistency than did those on the iron standards themselves." To assist in remedying this situation, Harrison [5] cleverly contrived a complicated machine for the rapid direct determination of wavelengths from Fabry-Perot interferometer patterns. He called this machine the WINMAC

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[1] Figures in brackets indicate the literature references at the end of this paper.

(Wavelength interferometric measurement and computation), and in 1950 he reported [6] that "the WINMAC is now being readied for what is hoped will be an extensive series of wavelength determinations of intermediate wavelength standards in cerium, thorium, and other elements." Unfortunately this hope did not materialize. However, this is not seriously regretted now because in the meantime great improvements over the traditional arcs and sparks at atmospheric pressure have been made in spectroscopic light sources.

The most simple, convenient, efficient, and economical type of spectroscopic light source is an evacuated tube of fused quartz enclosing a trace of gas, metal vapor, or volatile metallic compound excited by microwaves generated by vacuum-tube oscillators or by magnetrons. The prototype was the low pressure, water-cooled Hg^{198} lamp described by Meggers and Westfall [7], who also discovered that "clean-up" in such discharges varied inversely with frequency. In most laboratories magnetrons producing 2,450 Mc, or more, soon replaced vacuum-tube oscillators producing 100 to 300 Mc for the excitation of these lamps. The preparation of similar lamps with other volatile metals was described by Zelikoff, Wyckoff, Aschenbrand, and Loomis [8], while Corliss, Bozman, and Westfall [9] demonstrated that such lamps can be made to emit the spectra of all metals that form volatile compounds. A precise procedure for the preparation of electrodeless discharge tubes containing very pure rare earths and highly radioactive elements has been described by Tomkins and Fred [10]. Compared with conventional arcs and sparks, these lamps require a minimum amount of sample, which is enclosed and conserved. Also, they operate at relatively low temperature and pressure, and consequently emit spectral lines of greatly reduced width usually free of self-reversal. When operated with continuous wave power and moderate gas or vapor pressure, these lamps strongly favor the spectra of neutral atoms, but pulsed discharges and/or reduced pressures enhance the second and third spectra. Lamps viewed end-on when excited by a 100-watt magnetron emit spectra comparable in intensity to a 10-ampere 220-volt d-c arc, but with line widths much less than half as great. Bright, sharp lines are especially needed for the resolution of complex Zeeman patterns, or for the measurement of isotopic-spectroscopic effects. The development of these electrodeless lamps has thus greatly increased the range and precision of spectroscopic observations.

Now the accurate description and quantum interpretation of the spectra of rare-earth types of atoms and ions is still in a very unsatisfactory state, because of their extreme complexity and because pure samples have not been available in the past. The latter difficulty has recently been overcome either by efficient separation or by artificial preparation, but extreme complexity of the spectra remains as an obstacle to successful analysis. It is primarily for this reason that wavelengths must be measured with greater accuracy, and for this purpose reference standards of greater precision and better distribution than those from an iron arc are absolutely necessary. Fortunately the simple electrodeless lamps referred to provide the means for obtaining a greatly improved system of standard wavelengths [11]. Lamps containing a trace of a thorium halide excited by microwaves emit approximately 20,000 lines of uniformly sharp character and even distribution between 2000 and 12000 A. Since these lines are characteristic of heavy atoms and ions of even mass ($Z=90$, $A=232$) they have relatively small Doppler-Fizeau widths, and are entirely free from hyperfine structure or isotope shifts. By imaging a thorium-halide lamp inside a similar one containing Hg^{198} (or vice versa) both sources can be caused simultaneously to illuminate a Fabry-Perot interferometer and stigmatic spectrograph. From the interference patterns the wavelengths of thorium lines can then be determined to 8 figures relative to the previously determined values of the mercury lines. The purpose of this paper is to present preliminary results of such wavelength measurements for 222 radiations from thorium, covering slightly more than one octave of spectrum.

2. Light Sources

The thorium source used in this investigation was an electrodeless discharge tube containing a few milligrams of thorium iodide and pure helium gas at a pressure of 5 mm of Hg or less. The tube was prepared by C. H. Corliss in a manner previously described [9]. The tube blank is made of Vycor glass; it has a bore of approximately 5 mm and a length of 11.3 cm. The discharge was excited at a frequency of 2,450 Mc obtained from a commercial diathermy generator.

The thorium tube used throughout the investigation was chosen from among several that were made at the same time. After a warmup period of 30 to 60 sec, the tube would glow very brightly for approximately 3 min. At the end of this time the thorium spectrum would weaken, and the discharge would be confined to a narrow filament near the center of the tube, indicating that the pressure in the tube had increased. The period of high intensity mentioned above was accompanied by a gradual movement of the thorium iodide deposit from the top to the bottom of the tube. As soon as the thorium spectrum began to weaken, the discharge tube was removed from its holder, cooled in water, and replaced in an inverted position with the thorium iodide deposit again at the top of the tube. For many of the photographs, this 3-min running time was sufficient. For longer exposures it was necessary to cool and invert the tube several times. This change could be made within 30 sec.

The primary standard on which the thorium measurements were based was a NBS-Meggers Hg^{198} lamp [7], that contained 1 mg of Hg^{198} and argon at a pressure of approximately 3 mm of Hg. The mercury tube was excited by a second diathermy generator at the same frequency of 2,450 Mc. The Hg^{198} source was cooled by an air stream from a small blower.

3. Experimental Method

The optical arrangement was the same as that used by the authors in the previous investigation of iron wavelengths from an electrodeless tube [1]. For this reason, only a brief description will be given here. The Fabry-Perot interferometer consisted of aluminized quartz plates separated by 3 sets of invar pins either 25, 40, or 50 mm in length. Good interference fringes were also obtained with plate separation of 67.5 mm, but lack of time did not permit the exploitation of the higher orders of interference.

The evacuated ($<10^{-4}$ mm Hg) interferometer was mounted externally in parallel light. Both thorium and Hg^{198} lamps were placed on the optical axis but at right angles to it and parallel to the spectrograph slit, so that both sources were observed side-on. The Hg^{198} lamp was farther from the slit so that it could be imaged inside the thorium tube. From this point on, light from both lamps traveled the same path through condensing lens, interferometer, projection lens, and thence through the slit and spectrograph. The quartz-fluorite achromatic projection lens had the proper focal length (50 cm or 100 cm) to form six or more circular fringes on the spectrograph slit, which was 25 mm long and either 0.15 or 0.30 mm wide. Accuracy of measurement was thus favored by the large scale of the interference patterns and by a slit width that made the fringes approximate rectangles.

Dispersion in the horizontal direction was produced by a 15,000-line-per-inch concave grating in the Wadsworth mounting. The curvature of the plate holder was decreased so as to favor the horizontal focus and thus produce sharp images of the Fabry-Perot fringes from both lamps, simultaneously over as large a range as possible. This instrument was used to photograph diametral sections of interference patterns for waves between 4400 and 7000 A, with a slit width of 0.30 mm and a reciprocal dispersion of 5 A/mm in the first-order grating spectrum. Because of the higher density of lines in the ultraviolet spectrum of thorium, the region from 3275 to 4500 A was photographed in the second-order grating spectrum with a reciprocal dispersion of 2.45 A/mm and slit width of 0.15 mm. Under these conditions most of the measured interference patterns were free from overlaps of neighboring lines, but if many more thorium wavelengths are to be measured larger grating dispersion or smaller slit width will be necessary. In each wavelength range several spectrograms were made with different exposure times, and with slight mechanical-pressure changes in the interferometer spacing to alter the interference configurations or fractional orders for all spectral lines.

The interferometer plates were the same ones used previously for measurements of iron and mercury wavelengths [1, 12, 13]. The last series of measurements [13] suggested that the dispersion of phase change in the aluminum films was very small between 3300 and 6000 A, so no corrections on account of phase change were applied to these thorium wavelengths. No significant differences were found between results from the 25-, 40-, and 50-mm etalons.

All mercury lines that appeared with sufficient intensity were measured along with the thorium lines. The green (5462.2705 A) and violet (4047.7144 A) lines of Hg^{198} were chosen as standards respectively for the long- and short-wave interference spectrograms described above. The values of other Hg^{198} lines measured on these spectrograms agreed quite well with unpublished wavelengths [13], the greatest difference being 0.0002 A. This supports our assumption that any possible corrections to these thorium preliminary wavelengths on account of dispersion of phase-change in the interferometer films are negligible.

The interferograms were measured at the National Bureau of Standards with the interference comparator designed by K. Burns [14], and at Purdue University with a comparator made by Carl Leiss. In order to measure as many thorium wavelengths as possible within a given time, it was found desirable to measure just 5 diameters of each interference pattern. As mentioned before [7], by measuring the diameters of 5 interference rings, the least-squares evaluation of the fractional order at the center may be made with a minimum of arithmetical computation because some of the steps are easily performed mentally. Even with this conservation of time and labor the thorium wavelengths presented in this paper required the bisection of more than 12,000 interference fringes and calculations for more than 1,200 individual patterns.

Another way to reduce the time and labor involved in interferometric comparisons of wavelengths is to begin with the largest orders of interference consistent with finding the correct integral order for each line. If grating measurements of wavelength are to be refined and replaced by interferometric values, the initial orders of interference should not be so great that errors in the grating values lead to wrong integral orders. For example, if a thorium wavelength near 5000 A is to be measured relative to 5462.2705 A of Hg^{198}, the whole order of the thorium wavelength with a 25-mm etalon will be about 100,000, and the error in the grating value must be less than ± 0.02 A if it is to yield the correct integral order. We assumed that the available grating values of thorium wavelengths justified beginning the interferometric observations with a 25-mm etalon and then testing these values with a 40-mm etalon. If the integral orders of interference are in error because of too large errors in the grating values, the 25- and 40-mm etalon values will differ radically, but if the integral orders are correct, the results will agree within a very small possible error of observation. This bold procedure saved much time and labor by eliminating interferometric observations with all smaller etalons which do not contribute anything to the accuracy attainable with the larger etalons.

Two independent sets of grating values of thorium wavelengths were available, one in the *MIT Wavelength Tables* [2] representing wavelengths emitted by a thorium arc, and the second representing unpublished wavelengths from thorium halide lamps measured by R. Zalubas in the National Bureau of

TABLE 1. *Thorium wavelengths: grating and interferometer values*

	λ_{air}	λ_{vac}	λ_{vac} (25 mm)	Change in order	λ_{vac} (40 mm)
MIT	4165. 813	4166. 987	4166. 9750	----	4166. 9832
NBS	4165. 782	4166. 956	4166. 9403	+1	4166. 9403
MIT	3869. 639	3870. 736	3870. 7308	----	3870. 7416
NBS	3869. 665	3870. 762	3870. 7606	−1	3870. 7604
MIT	3854. 547	3855. 640	3855. 6333	----	3855. 6222
NBS	3854. 512	3855. 605	3855. 6036	+1	3855. 6035
MIT	3421. 189	3422. 170	3422. 1673	----	3422. 1618
NBS	3421. 215	3422. 196	3422. 1908	−1	3422. 1910

Standards. Both sets were referred to the adopted secondary standards of wavelength obtained from the iron arc at atmospheric pressure. We gave preference to the MIT grating values because these were objectively measured and calculated by automatic machines [2], and therefore entirely free from human errors. This was a mistake; the only errors in integral orders of 25-mm etalons occurred because of errors larger than 0.02 A in the MIT grating values as shown in table 1. The first line shows in succession the MIT wavelength in air, its value in vacuum [15], and discordant results from 25-mm etalons and from 40-mm etalons. The second line gives similar data for NBS grating wavelengths, but the results from 25- and 40-mm etalons are in perfect agreement because the integral orders were corrected as indicated by the NBS grating values. The interferometric values for these four lines show that the MIT grating values have errors of +0.047, −0.025, +0.036, and −0.021 A, respectively, whereas the NBS errors are +0.016, +0.001, +0.001, and +0.005 A. No explanation of the large and erratic errors in the MIT grating values is offered, but this experience should be a warning that some 7-figure MIT wavelengths may not be trustworthy beyond 5 figures.

4. Results

The thorium wavelengths obtained as a result of this investigation are presented in table 2. Since the interferometer was evacuated and the separation of the interferometer plates was always expressed in terms of vacuum wavelengths of Hg^{198} standards, all the measured wavelengths of thorium are valid only in vacuum. Column 1 displays only that part of the vacuum wavelength that can be expressed in whole angstroms, the fraction that must be added to this is given in columns 2, 3, and 4, depending on whether it was measured respectively with 25-, 40-, or 50-mm etalons. A figure in parentheses following each fraction shows the number of individual determinations. Column 5 contains the average preliminary vacuum wavelength resulting from all the observations. In column 6 the vacuum wavelenghts of column 5 are changed to values in standard air with the aid of Edlén's conversion table [15]. Column 7 quotes unpublished estimated relative intensities of thorium lines as given by Zalubas, and column 8 indicates the particular spectrum to which each wavelength belongs.

It is a common characteristic of all complex spectra that neutral atoms dominate the visible, and singly-ionized atoms predominate in the ultraviolet. In these preliminary measurements of thorium wavelengths with Fabry-Perot etalons no difference in character could be observed between the Th I and Th II lines, and there is no reason to suspect that one category is more accurately measured than the other. Unfortunately none of the thorium wavelengths has been measured a sufficient number of times with any given etalon to compute a meaningful probable error or standard deviation. A considerable number of the wavelengths from a given etalon are limited to a single observation and a comparison of these with the over-all averages may give an impression of the uncertainty in individual observations.

Because of the lack of sufficient observational material to calculate probable errors of the thorium wavelengths, an attempt was made to test their relative values by means of the combination principle. Although the Th II spectrum has been extensively analyzed [16] no recurring wavenumber differences were found between Th II lines in table 2. Somewhat better fortune was encountered with Th I lines. Even though the published analysis of Th I is extremely fragmentary [17] it is now being extended by Zalubas [18] who has reported that 27 of our interferometric values of Th I lines test the constancy of 4 wavenumber differences, viz., 2869.261, 3687.990, 5563.143, and 6362.396 K ($=cm^{-1}$) between low-energy levels established for neutral thorium atoms. These are presented in table 3 as 14 pairs of vacuum wavelengths in A, and their reciprocals, or vacuum wavenumbers in K. The mean deviation of the 14 differences from their arithmetical averages is 0.001_2 K, that is 1 part in about 20 million. The pairs numbered 2 and 3 account for two-thirds of the summed deviations; if these are ignored the remaining 12 exhibit an average departure of only 0.0005 K, or 1 part in about 40 million, but this may be discounted as accidental.

The 222 wavelengths (3288.7356 to 6991.5839 A) of thorium radiations in table 2 are presented as a preliminary set of improved standard wavelengths for the measurement of highly-dispersed complex spectra. The average interval between these stand-

TABLE 2. *Wavelengths in thorium spectra*

1	2	3	4	5	6	7	8
Whole angstrom	Fractional angstrom			Vacuum	Air	Relative intensity	Spectrum
	25 mm(obs.)	40 mm(obs.)	50 mm(obs.)				
6991	5840 (2)	5839 (3)	5839 (1)	6991. 5839	6989. 6562	900	I
6945	5265 (3)	5266 (3)	5263 (1)	6945. 5265	6943. 6112	600	I
6913	1334 (3)	1338 (3)	1333 (1)	6913. 1336	6911. 2264	400	I
6836	8110 (4)	8114 (2)	8108 (1)	6836. 8110	6834. 9249	75	I
6830	9196 (2)	9205 (1)	9201 (1)	6830. 9200	6829. 0355	150	I
6758	3179 (3)	3178 (2)	3176 (1)	6758. 3178	6756. 4528	250	I
6729	3153 (2)	3161 (1)	3162 (1)	6729. 3157	6727. 4585	200	I
6680	--------	5511 (1)	5522 (1)	6680. 5516	6678. 7076	30	I
6664	1088 (4)	1089 (3)	1094 (1)	6664. 1090	6662. 2694	250	I
6660	--------	5161 (1)	5161 (1)	6660. 5161	6658. 6774	50	I
6595	7610 (4)	7610 (3)	7608 (1)	6595. 7610	6593. 9397	200	I
6593	--------	3059 (1)	3051 (1)	6593. 3055	6591. 4849	100	I
6590	3595 (4)	3600 (2)	3596 (1)	6590. 3596	6588. 5398	200	I
6585	7248 (4)	7254 (3)	7251 (1)	6585. 7251	6583. 9065	200	I
6555	9715 (2)	9710 (4)	9707 (1)	6555. 9711	6554. 1605	100	I
6533	1468 (5)	1465 (4)	1466 (1)	6533. 1467	6531. 3423	400	I
6492	5317 (2)	5312 (4)	5313 (1)	6492. 5313	6490. 7378	120	I
6459	0675 (4)	0678 (3)	0680 (1)	6459. 0677	6457. 2834	500	I
6415	--------	3881 (3)	3876 (1)	6415. 3880	6413. 6152	200	I
6413	6717 (4)	6721 (4)	6719 (1)	6413. 6719	6411. 8996	250	I
6378	6939 (3)	6940 (4)	6933 (1)	6378. 6939	6376. 9310	350	I
6344	6134 (4)	6143 (4)	6135 (1)	6344. 6138	6342. 8600	300	I
6329	0286 (2)	0285 (4)	0270 (1)	6329. 0284	6327. 2788	180	I
6263	1499 (4)	1493 (4)	1504 (1)	6263. 1496	6261. 4177	180	I
6259	1546 (3)	1546 (3)	1548 (1)	6259. 1546	6257. 4237	100	I
6226	2497 (2)	2494 (4)	2494 (1)	6226. 2495	6224. 5275	100	I
6208	9379 (5)	9380 (4)	9378 (1)	6208. 9379	6207. 2205	160	I
6193	--------	6188 (1)	6186 (1)	6193. 6187	6191. 9054	100	I
6184	3324 (4)	3331 (4)	3326 (1)	6184. 3327	6182. 6219	400	I
6153	6954 (5)	6962 (3)	6959 (1)	6153. 6958	6151. 9932	120	I
6104	2838 (2)	2837 (2)	2849 (1)	6104. 2839	6102. 5946	90	I
6089	7161 (2)	7159 (2)	7160 (1)	6089. 7160	6088. 0306	125	I
6087	0592 (5)	0596 (2)	0586 (1)	6087. 0592	6085. 3745	100	I
6050	7258 (2)	7259 (2)	7259 (1)	6050. 7259	6049. 0510	100	I
6039	3696 (5)	3700 (4)	3696 (1)	6039. 3697	6037. 6978	140	I
6022	7042 (1)	7038 (2)	--------	6022. 7040	6021. 0362	140	I
6008	7362 (4)	7361 (4)	7364 (1)	6008. 7362	6007. 0725	180	I
5976	7202 (2)	7208 (4)	7213 (1)	5976. 7207	5975. 0656	250	I
5975	3202 (5)	3196 (4)	3193 (1)	5975. 3199	5973. 6651	250	I
5940	4710 (4)	4708 (4)	4708 (1)	5940. 4709	5938. 8255	140	I
5887	3325 (1)	3331 (1)	3329 (1)	5887. 3329	5885. 7017	120	I
5854	3043 (4)	3033 (2)	3053 (1)	5854. 3040	5852. 6817	200	I
5805	7508 (5)	7507 (4)	7509 (1)	5805. 7508	5804. 1414	300	I
5792	2686 (5)	2686 (3)	2683 (1)	5792. 2686	5790. 6629	------	Hg^{198}
5791	2494 (3)	2495 (2)	2492 (1)	5791. 2494	5789. 6439	200	I
5771	1983 (5)	1983 (4)	1980 (1)	5771. 1983	5769. 5982	------	Hg^{198}
5762	1484 (4)	1489 (4)	1489 (1)	5762. 1487	5760. 5510	600	I
5726	9766 (1)	9771 (3)	--------	5726. 9770	5725. 3887	250	I
5708	6864 (4)	6870 (4)	6872 (1)	5708. 6867	5707. 1033	200	II
5659	--------	4963 (1)	4958 (1)	5659. 4960	5657. 9258	100	I
5641	3109 (3)	3122 (3)	3120 (1)	5641. 3115	5639. 7461	250	II
5616	8789 (2)	8790 (4)	--------	5616. 8790	5615. 3202	350	I
5588	5775 (5)	5780 (5)	5781 (1)	5588. 5778	5587. 0265	500	I
5580	9073 (3)	9080 (4)	9080 (1)	5580. 9077	5579. 3585	300	I
5574	9014 (4)	9015 (4)	9010 (1)	5574. 9014	5573. 3538	350	I
5559	8862 (3)	8862 (4)	8859 (1)	5559. 8862	5558. 3426	400	I
5549	7171 (4)	7169 (3)	7172 (1)	5549. 7170	5548. 1761	300	I
5540	8001 (5)	8000 (5)	7999 (1)	5540. 8000	5539. 2615	400	I
5511	5243 (4)	5247 (4)	5238 (1)	5511. 5244	5509 9937	300	I
5500	7828 (5)	7831 (5)	7831 (1)	5500. 7830	5499. 2552	250	I

TABLE 2. *Wavelengths in thorium spectra*—Continued

1	2	3	4	5	6	7	8
Whole angstrom	Fractional angstrom			Vacuum	Air	Relative intensity	Spectrum
	25 mm(obs.)	40 mm(obs.)	50 mm(obs.)				
5462	2705 (5)	2705 (5)	2705 (1)	5462. 2705	5460. 7530	------	Hg 198
5453	7338 (1)	7343 (2)	--------	5453. 7341	5452. 2188	250	I
5432	6213 (4)	6211 (2)	6216 (1)	5432. 6212	5431. 1116	300	I
5427	1859 (2)	1865 (3)	--------	5427. 1863	5425. 6781	250	II
5418	9915 (5)	9916 (5)	9916 (1)	5418. 9916	5417. 4856	200	I
5409	1568 (4)	1570 (3)	1573 (1)	5409. 1569	5407. 6535	200	I
5388	1093 (1)	1083 (1)	1087 (1)	5388. 1087	5386. 6109	300	I
5345	0672 (3)	0678 (3)	0681 (1)	5345. 0676	5343. 5813	500	I
5328	4573 (3)	4575 (3)	4572 (1)	5328. 4574	5326. 9755	400	I
5278	9691 (2)	9687 (2)	--------	5278. 9689	5277. 5002	400	II
5259	8245 (3)	8245 (3)	--------	5259. 8245	5258. 3609	300	I
5232	6158 (3)	6160 (3)	--------	5232. 6159	5231. 1596	900	I
5178	4028 (3)	4023 (3)	--------	5178. 4025	5176. 9606	400	I
5160	0408 (3)	0413 (3)	--------	5160. 0411	5158. 6041	700	I
5155	6781 (1)	6789 (3)	--------	5155. 6787	5154. 2429	400	I
5116	4694 (2)	4700 (2)	--------	5116. 4697	5115. 0443	250	I
5069	3865 (2)	3870 (2)	--------	5069. 3868	5067. 9739	900	I
5051	2039 (2)	2039 (2)	--------	5051. 2039	5049. 7959	400	II
5030	0581 (2)	0594 (2)	--------	5030. 0588	5028. 6564	400	II
5018	6537 (3)	6542 (2)	--------	5018. 6539	5017. 2545	500	II
5003	4922 (3)	4922 (2)	--------	5003. 4922	5002. 0968	400	I
4941	0205 (4)	0204 (2)	--------	4941. 0205	4939. 6417	350	I
4921	1894 (3)	1886 (2)	--------	4921. 1890	4919. 8155	600	II
4896	3214 (4)	3216 (2)	--------	4896. 3215	4894. 9546	350	I
4880	0950 (2)	0965 (1)	--------	4880. 096	4878. 733	200	I
4866	8360 (2)	8360 (1)	--------	4866. 8360	4865. 4769	350	I
4864	5306 (3)	5309 (1)	--------	4864. 5307	4863. 1722	1000	II
4842	1949 (2)	1953 (2)	--------	4842. 1951	4840. 8426	400	I
4809	4775 (3)	4770 (2)	--------	4809. 4773	4808. 1334	350	I
4790	7254 (3)	7259 (2)	--------	4790. 7256	4789. 3867	300	I
4767	9328 (2)	9334 (1)	--------	4767. 9330	4766. 6001	200	I
4753	7427 (2)	7432 (2)	--------	4753. 7430	4752. 4139	500	II
4705	3059 (3)	3060 (2)	--------	4705. 3060	4703. 9897	500	I
4687	5062 (2)	5055 (1)	--------	4687. 5060	4686. 1944	1200	I
4674	9691 (2)	9689 (2)	--------	4674. 9690	4673. 6608	600	I
4669	4787 (3)	4789 (2)	--------	4669. 4788	4668. 1720	700	I
4664	5076 (1)	5076 (2)	--------	4664. 5076	4663. 2021	200	I
4633	0584 (3)	0583 (2)	--------	4633. 0583	4631. 7611	1100	I
4596	7072 (3)	7085 (1)	--------	4596. 7074	4595. 4198	600	I
4589	7122 (2)	7124 (1)	--------	4589. 7123	4588. 4266	400	I
4572	2522 (2)	2533 (1)	--------	4572. 2526	4570. 9715	500	I
4557	0912 (2)	0890 (1)	--------	4557. 090	4555. 813	500	I
4536	5251 (2)	5266 (1)	--------	4536. 526	4535. 254	300	I
4511	7906 (3)	7910 (2)	--------	4511. 7908	4510. 5257	800	II
4494	5941 (3)	5942 (2)	--------	4494. 5941	4493. 3335	1200	I
4483	4270 (3)	4269 (2)	--------	4483. 4270	4482. 1694	300	I
4466	5936 (3)	5940 (3)	--------	4466. 5938	4465. 3406	300	II
4459	2531 (5)	2530 (3)	--------	4459. 2531	4458. 0018	600	I
4446	5562 (2)	5561 (2)	--------	4446. 5561	4445. 3082	300	I
4434	2074 (4)	2076 (2)	--------	4434. 2075	4432. 9628	600	II
4410	1211 (5)	1210 (3)	--------	4410. 1211	4408. 8828	600	I
4404	1635 (5)	1641 (3)	--------	4404. 1637	4402. 9270	400	I
4402	8179 (1)	8183 (1)	--------	4402. 8181	4401. 5817	400	I
4392	3440 (7)	3440 (2)	--------	4392. 3440	4391. 1104	3000	II
4383	0917 (5)	0915 (2)	--------	4383. 0916	4381. 8604	900	I

TABLE 2. *Wavelengths in thorium spectra*—Continued

1	2	3	4	5	6	7	8
Whole angstrom	Fractional angstrom			Vacuum	Air	Relative intensity	Spectrum
	25 mm(obs.)	40 mm(obs.)	50 mm(obs.)				
4379	4069 (5)	4072 (2)	---------	4379. 4070	4378. 1768	500	I
4375	3535 (2)	3538 (1)	---------	4375. 3536	4374. 1244	600	I
4367	1572 (5)	1575 (2)	---------	4367. 1573	4365. 9303	600	I
4359	5624 (4)	5624 (3)	---------	4359. 5624	4358. 3374	------	Hg^{198}
4343	4765 (4)	4760 (2)	---------	4343. 4763	4342. 2555	300	I
4332	0620 (3)	0617 (1)	---------	4332. 0619	4330. 8441	300	I
4319	6302 (1)	6307 (1)	---------	4319. 6305	4318. 4160	700	I
4316	4681 (3)	4681 (2)	---------	4316. 4681	4315. 2544	400	I
4308	3878 (3)	3878 (2)	---------	4308. 3878	4307. 1763	700	I
4301	0490 (3)	0486 (1)	---------	4301. 0489	4299. 8393	600	I
4293	0176 (3)	0178 (2)	---------	4293. 0177	4291. 8102	400	I
4278	5178 (3)	5181 (2)	---------	4278. 5179	4277. 3142	1200	II
4274	5599 (3)	5603 (2)	---------	4274. 5600	4273. 3574	1000	II
4258	6946 (3)	6941 (2)	---------	4258. 6944	4257. 4959	700	I
4236	6563 (3)	6560 (1)	---------	4236. 6562	4235. 4635	600	I
4231	6183 (3)	6180 (1)	---------	4231. 6182	4230. 4268	600	I
4216	0152 (2)	0161 (1)	---------	4216. 0156	4214. 8283	200	I
4210	0766 (3)	0762 (2)	---------	4210. 0764	4208. 8907	3000	II
4194	1981 (3)	1980 (2)	---------	4194. 1980	4193. 0165	900	I
4179	2375 (3)	2374 (2)	---------	4179. 2374	4178. 0598	3000	II
4166	9403 (3)	9403 (2)	---------	4166. 9403	4165. 7659	1000	I
4159	7078 (3)	7074 (2)	---------	4159. 7076	4158. 5351	800	I
4151	1566 (3)	1570 (2)	---------	4151. 1568	4149. 9865	800	II
4133	9191 (3)	9191 (1)	---------	4133. 9191	4132. 7534	600	II
4128	5761 (3)	5759 (2)	---------	4128. 5760	4127. 4117	1400	I
4116	9199 (3)	9201 (2)	---------	4116. 9200	4115. 7587	800	I
4109	5788 (3)	5791 (1)	---------	4109. 5789	4108. 4195	800	II
4101	4985 (3)	4984 (2)	---------	4101. 4984	4100. 3412	1100	I
4095	9025 (3)	9031 (2)	---------	4095. 9028	4094. 7470	1600	II
4087	6743 (2)	6739 (2)	---------	4087. 6741	4086. 5205	1600	II
4068	5993 (3)	5992 (2)	---------	4068. 5993	4067. 4507	400	I
4060	3990 (3)	3991 (2)	---------	4060. 3990	4059. 2525	1000	I
4047	7144 (3)	7144 (2)	---------	4047. 7144	4046. 5712	------	Hg^{198}
4044	5366 (3)	5371 (2)	---------	4044. 5368	4043. 3945	800	I
4037	1880 (3)	1878 (2)	---------	4037. 1879	4036. 0475	1800	I
4020	2649 (4)	2649 (2)	---------	4020. 2649	4019. 1289	4000	II
4013	6295 (3)	6292 (2)	---------	4013. 6293	4012. 4950	2000	I
4009	3433 (3)	3438 (2)	---------	4009. 3435	4008. 2104	1600	I
3995	6786 (3)	6787 (2)	---------	3995. 6786	3994. 5490	1200	I
3981	2147 (3)	2153 (2)	---------	3981. 2150	3980. 0892	1100	I
3968	5145 (3)	5142 (2)	---------	3968. 5144	3967. 3919	2000	I
3950	0814 (2)	0810 (1)	---------	3950. 0813	3948. 9636	1000	I
3934	0243 (3)	0243 (1)	---------	3934. 0243	3932. 9108	1400	I
3924	9103 (3)	9106 (1)	---------	3924. 9104	3923. 7993	400	I
3906	2992 (2)	2926 (1)	---------	3906. 2924	3905. 1861	1500	II
3870	7606 (2)	7604 (2)	---------	3870. 7605	3869. 6635	600	I
3864	5008 (3)	5011 (2)	---------	3864. 5009	3863. 4055	1200	II
3855	6036 (3)	6035 (2)	---------	3855. 6036	3854. 5105	1200	II
3843	0497 (3)	0499 (2)	---------	3843. 0498	3841. 9600	1200	II
3840	7829 (3)	7837 (2)	---------	3840. 7833	3839. 6941	2500	I
3829	4707 (3)	4709 (2)	---------	3829. 4708	3828. 3845	3200	I
3819	7691 (1)	7692 (1)	---------	3819. 7692	3818. 6855	500	I
3814	1497 (3)	1497 (2)	---------	3814. 1497	3813. 0674	1200	II
3804	1545 (3)	1550 (2)	---------	3804. 1547	3803. 0750	4000	I
3786	6748 (1)	6749 (1)	---------	3786. 6749	3785. 5997	1000	II

TABLE 2. *Wavelengths in thorium spectra*—Continued

1	2	3	4	5	6	7	8
Whole angstrom	Fractional angstrom			Vacuum	Air	Relative intensity	Spectrum
	25 mm(obs.)	40 mm(obs.)	50 mm(obs.)				
3782	0398 (1)	0405 (1)	--------	3782. 0402	3780. 9663	350	I
3772	4418 (3)	4418 (2)	--------	3772. 4418	3771. 3703	1500	I
3764	0037 (3)	0027 (2)	--------	3764. 0032	3762. 9345	1200	I
3753	6349 (3)	6353 (2)	--------	3753. 6351	3752. 5685	3500	II
3743	9871 (3)	9873 (2)	--------	3743. 9872	3742. 9231	1100	I
3728	9626 (3)	9622 (1)	--------	3728. 9624	3727. 9022	800	I
3720	4924 (3)	4926 (1)	--------	3720. 4925	3719. 4345	3000	I
3712	3595 (2)	3597 (2)	--------	3712. 3596	3711. 3037	600	II
3702	0310 (3)	0313 (2)	--------	3702. 0312	3700. 9780	300	I
3693	6171 (3)	6171 (2)	--------	3693. 6171	3692. 5661	1200	I
3683	5343 (3)	5347 (2)	--------	3683. 5345	3682. 4861	1000	I
3671	0137 (1)	0141 (1)	--------	3671. 0139	3669. 9687	750	I
3669	1842 (3)	1844 (2)	--------	3669. 1843	3668. 1396	1000	I
3657	7352 (3)	7354 (2)	--------	3657. 7353	3656. 6936	1000	I
3651	1962 (2)	1971 (1)	--------	3651. 1967	3650. 1566	------	Hg^{198}
3643	2866 (3)	2867 (2)	--------	3643. 2867	3642. 2487	2200	I
3633	8656 (3)	8654 (2)	--------	3633. 8655	3632. 8299	1000	I
3623	8282 (3)	8280 (2)	--------	3623. 8281	3622. 7951	800	I
3616	1633 (1)	1634 (1)	--------	3616. 1634	3615. 1324	2000	II
3613	4575 (3)	4573 (2)	--------	3613. 4574	3612. 4271	1400	I
3599	1459 (3)	1464 (2)	--------	3599. 1462	3598. 1196	2000	I
3593	8040 (3)	8042 (2)	--------	3593. 8041	3592. 7788	2000	I
3585	1985 (2)	1981 (2)	--------	3585. 1983	3584. 1753	800	I
3577	5786 (3)	5782 (2)	--------	3577. 5784	3576. 5573	1000	II
3568	2818 (3)	2825 (2)	--------	3568. 2822	3567. 2635	1200	I
3560	4658 (1)	4657 (1)	--------	3560. 4657	3559. 4490	2500	II
3552	4161 (3)	4158 (2)	--------	3552. 4159	3551. 4013	1000	I
3545	0306 (3)	0300 (2)	--------	3545. 0303	3544. 0176	1500	I
3540	5980 (3)	5983 (2)	--------	3540. 5982	3539. 5867	4000	II
3519	4094 (3)	4095 (2)	--------	3519. 4094	3518. 4033	1000	I
3512	1610 (3)	1613 (2)	--------	3512. 1612	3511. 1570	1000	I
3504	7880 (1)	7870 (1)	--------	3504. 7875	3503. 7852	500	I
3499	6215 (3)	6216 (2)	--------	3499. 6216	3498. 6206	900	I
3494	5174 (2)	5174 (1)	--------	3494. 5174	3493. 5177	2000	II
3480	1680 (3)	1688 (1)	--------	3480. 1683	3479. 1723	800	II
3469	2126 (3)	2125 (2)	--------	3469. 2125	3468. 2193	2000	II
3463	8419 (2)	8417 (2)	--------	3463. 8418	3462. 8500	2000	II
3452	6910 (3)	6908 (2)	--------	3452. 6909	3451. 7019	900	I
3443	5652 (3)	5651 (2)	--------	3443. 5651	3442. 5785	800	I
3434	9827 (3)	9831 (2)	--------	3434. 9829	3433. 9985	3000	II
3422	1908 (3)	1910 (2)	--------	3422. 1909	3421. 2097	2500	I
3413	9918 (3)	9918 (2)	--------	3413. 9918	3413. 0127	1800	I
3406	5346 (3)	5348 (2)	--------	3406. 5347	3405. 5575	1400	I
3397	7021 (3)	7022 (2)	--------	3397. 7022	3396. 7273	1400	I
3393	0083 (1)	0087 (1)	--------	3393. 0085	3392. 0348	6000	II
3386	5033 (3)	5030 (2)	--------	3386. 5032	3385. 5312	800	II
3381	8300 (3)	8305 (2)	--------	3381. 8303	3380. 8595	900	I
3375	9438 (3)	9440 (2)	--------	3375. 9439	3374. 9746	1600	I
3359	5663 (3)	5668 (3)	--------	3359. 5666	3358. 6014	2000	II
3352	1910 (3)	1913 (2)	--------	3352. 1911	3351. 2278	2500	II
3338	8296 (3)	8297 (2)	--------	3338. 8296	3337. 8697	2000	II
3331	4347 (2)	4343 (1)	--------	3331. 4345	3330. 4765	1800	I
3326	0765 (3)	0768 (2)	--------	3326. 0767	3325. 1201	3000	II
3325	7088 (3)	7088 (2)	--------	3325. 7088	3324. 7523	2000	II
3310	3174 (3)	3180 (2)	--------	3310. 3176	3309. 3650	800	I
3305	1894 (3)	--------	--------	3305. 1894	3304. 2381	3000	I
3293	4685 (3)	4686 (1)	--------	3293. 4685	3292. 5202	3000	II
3288	7355 (3)	7357 (2)	--------	3288. 7356	3287. 7885	1600	II

TABLE 3. *Test of Th I wavelengths*

Line pair	Wavelength	Wavenumber	Wavenumber difference
	A	K	K
1	4494. 5941 5160. 0411	22248. 950 19379. 690	2869. 260
2	4375. 3536 5003. 4922	22855. 296 19986. 041	2869. 255
3	3840. 7833 4316. 4681	26036. 356 23167. 089	2869. 267
4	3643. 2867 4068. 5993	27447. 744 24578. 483	2869. 261
5	3599. 1462 4013. 6293	27784. 367 24915. 106	2869. 261
6	3331. 4345 3683. 5345	30017. 099 27147. 838	2869. 261
7	3310. 3176 3657. 7353	30208. 582 27339. 321	2869. 261
8	4896. 3215 5975. 3199	20423. 495 16735. 506	3687. 989
9	3829. 4708 4459. 2531	26113. 269 22425. 280	3687. 989
10	3305. 1894 3764. 0032	30255. 452 26567. 459	3687. 993
11	4896. 3215 6729. 3157	20423. 495 14860. 352	5563. 143
12	4258. 6944 5580. 9077	23481. 375 17918. 232	5563. 143
13	4104. 4984 5549. 7170	24381. 333 18018. 937	6362. 396
14	4037. 1879 5432. 6212	24769. 716 18407. 320	6362. 396

ards is 10 A from 3300 to 4300 A, 17 A from 4300 to 5300 A, 23 A from 5300 to 6300 A, and 30 A from 6300 to 7000 A. This distribution according to wavelength corresponds closely to an average spacing of standards at intervals of 72 K on a wavenumber scale throughout the range 14300 to 30400 K. Since spectra are always measured in wavelength units, but interpreted in wavenumber units (proportional to energy) this is suggested as the ideal distribution of secondary standards of wavelength. It is emphasized again that the values in table 2 are only a preliminary list which should be refined by comparing still higher orders of interference, and perhaps measuring still more wavelengths to decrease the intervals between standards.

The present list of 222 thorium wavelengths in table 2 may serve for immediate direct measurement of complex spectra from 3300 to 7000 A, and by photographing these standards in a grating's second-order spectrum and doubling the values, they may serve also for the measurement of spectra from 6600 to 14000 A photographed in the grating's first order.

Finally, the most important next step is to extend the measurement of wavelengths from thorium-halide lamps to shorter waves, that is from 3300 to 2000 A or less. When this is done the iron arc at atmospheric pressure may be abandoned as a source of standard wavelengths (except for rough measurements) but still retained as an aid in recognizing the thorium standards. Because of the highly complex character of thorium spectra, and the lack of striking groups of lines or useful maps, it will be convenient (and perhaps necessary) to juxtapose the simpler and more familiar spectrum of the iron arc for purposes of orientation.

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